ROTATIONAL CORRECTION ON THE MORSE POTENTIAL THROUGH THE PEKERIS APPROXIMATION AND NIKIFOROV-UVAROV METHOD

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Abstract

The Nikiforov-Uvarov method is employed to calculate the the Schrödinger equation with a rotation Morse potential. The bound state energy eigenvalues and the corresponding eigenfunction are obtained. All of these calculation present an effective and clear method under a Pekeris approximation to solve a rotation Morse model. Meanwhile the results got here are in a good agreement with ones before.

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1   Introduction

As an empirical potential, the Morse potential has been one of most useful and convenient model. The Morse potential gives a excellent qualitative description of the interaction between the two atoms in a diatomic molecule and also it is a reasonable qualitative description of the interaction close to the surface [1]. For this potential, the Schrödinger equation shall be solved for the angular momentum quantum number l is equal to zero. As we know the rotation energy of a molecule is much smaller than that of vibration, and therefore in a pure Morse potential model the rotation energy of a molecule has been omitted. However, in some case, it is needed to be included if one wants to obtain analytical or semianalytical solutions to the Schrödinger equation. Then we will get a rotation Morse potential. Our interest is how to get the solution of Schrödinger equation for the rotation Morse potential.

In the previous reports, several approximations have been developed to find better analytical formulas for the rotating Morse potential [2]. Some of them require the calculation of a state-dependent internuclear distance through the numerical solutions of transcendental equations. Recently, an alternative method known as the Nikiforov-Uvarov (NU) method is introduced for solving the Schrödinger equation. The application of the method is to solve Schrödinger equation with some well-known potentials and to solve Dirac, Klein-Gordon and Duffin-Kemmer-Petiau equation for a Coulomb type potential. In the present work, the energy and the corresponding eigenfunctions are calculated employing the NU method under a Pekeris approximation [3].

2   Basic Equations of Nikiforov-Uvarov Method

The NU method provides us an exact solution of non−relativistic Schrödinger equation for certain kind of potentials [4]. The method is based on the solutions of general second order linear differential equation with special orthogonal functions [5]. For a given real or complex potential, the Schrödinger equation in one dimension is reduced to a generalized equation of hypergeometric type with an appropriate $s = s(x)$ coordinate transformation. Thus it can be written in the following form,

$$\psi''(s) + \frac{\widetilde{\tau}\,(s)}{\sigma}\psi'(s) + \frac{\widetilde{\sigma}\,(s)}{\sigma^2(s)}\psi(s) = 0 \tag{1}$$

where $\sigma(s)$ and $\widetilde{\sigma}\,(s)$ are polynomials, at most second−degree, and $\widetilde{\tau}\,(s)$ is a first−degree polynomial. To find a particular solution of Eq.(1) by separation of variables, we use the following the transformation

$$\psi(s) = \phi(s)y(s) \tag{2}$$

This reduces Schrödinger equation, Eq.(1), to an equation of hypergeometric type,

$$\sigma(s)y'' + \tau(s)y' + \lambda y = 0, \tag{3}$$

where $\phi(s)$ satisfies $\phi(s)'/\phi(s) = \pi(s)/\sigma(s)$. $y(s)$ is the hypergeometric type function whose polynomial solutions are given by Rodrigues relation

$$y_n(s) = \frac{B_n}{\rho(s)} \frac{d^n}{ds^n} \left[\sigma^n(s)\rho(s) \right], \tag{4}$$

where B_n is a normalizing constant and the weight function ρ must satisfy the condition [4]

$$(\sigma\rho)' = \tau\rho. \tag{5}$$

The function π and the parameter λ required for this method are defined as

$$\pi = \frac{\sigma' - \tilde{\tau}}{2} \pm \sqrt{\left(\frac{\sigma' - \tilde{\tau}}{2}\right)^2 - \tilde{\sigma} + k\sigma} \tag{6}$$

and

$$\lambda = k + \pi'. \tag{7}$$

Here, $\pi(s)$ is a polynomial with the parameter s and the determination of k is the essential point in the calculation of $\pi(s)$. Thus, in order to find the value of k, the expression under the square root must be square of a polynomial. Hence, a new eigenvalue equation for the Schrödinger equation becomes

$$\lambda = \lambda_n = -n\tau' - \frac{n(n-1)}{2}\sigma'', \quad (n = 0, 1, 2, ...) \tag{8}$$

where

$$\tau(s) = \tilde{\tau}(s) + 2\pi(s), \tag{9}$$

and it will have a negative derivative.

3   Rotational Correction on the Morse Potential

Consider a diatomic molecule system with reduced mass μ in the Morse potential

$$V(r) = D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] \qquad (D > 0, a > 0), \tag{10}$$

where D is dissociation energy, r_0 is the equilibrium bond length and a is a parameter controlling the width of the potential well. The vibrations of a two-atomic molecule can be excellently described by this potential type and solved bound states for $l = 0$. If one want

to obtain the solution of $l \neq 0$, the centrifugal term has to be attached to the potential in the Schrödinger radial equation. In this case, total potential shape becomes as follows

$$V_{total}(r) = D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] + \frac{\hbar^2 l(l+1)}{2\mu r^2}, \tag{11}$$

defining as the sum of the Morse potential and the centrifugal barrier. In order to calculate the energy eigenvalues and the corresponding eigenfunction, the potential function given by Eq.(10) is inserted into the radial Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + D[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] + \frac{\hbar^2 l(l+1)}{2\mu r^2}\right) R_{nl}(r) = E_{nl}R_{nl}(r). \tag{12}$$

An analytical exact solution of this differential equation cannot be found without an approximation. For this case, we now outline the procedure of Pekeris [3, 6].

3.1   Overview of the Pekeris Approximation

The approximation is based on the expansion of the centrifugal barrier in a series of exponentials depending on the internuclear distance, until the second order. However, by construction, this approximation is valid only for lower vibrational energy states. Therefore, for a Pekeris approximation, we can take care of the rotational term in the following way. We let $x = (r - r_0)/r_0$ and around $x = 0$ it may be expanded into a series of powers as

$$V_{rot}(x) = \frac{\gamma}{(1+x)^2} = \gamma(1 - 2x + 3x^2 - 4x^3 + ...), \tag{13}$$

with

$$\gamma = \frac{\hbar^2}{2\mu}\frac{l(l+1)}{r_0^2}, \tag{14}$$

the first few terms should be quite sufficient. Instead, we now replace the rotational term by the potential

$$\tilde{V}_{rot}(x) = \gamma\left(D_0 + D_1 e^{-\alpha x} + D_2 e^{-2\alpha x}\right), \tag{15}$$

where $\alpha = ar_0$. Combining equal powers of Eqs.(13) and (15) we get

$$\tilde{V}_{rot}(x) = \gamma\left(D_0 + D_1(1 - \alpha x + \frac{\alpha^2 x^2}{2!} - \frac{\alpha^3 x^3}{3!} + ...) + D_2(1 - 2\alpha x + \frac{4\alpha^2 x^2}{2!} - \frac{8\alpha^3 x^3}{3!} + ...)\right), \tag{16}$$

$$\tilde{V}_{rot}(x) = \gamma\left(D_0 + D_1 + D_2 - x(D_1\alpha + 2D_2\alpha) + x^2(D_1\frac{\alpha^2}{2} + 2D_2\alpha^2) - x^3(D_1\frac{\alpha^3}{6} + D_2\frac{4\alpha^3}{3}) + ...\right), \tag{17}$$

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where

$$D_0 = 1 - \frac{3}{\alpha} + \frac{3}{\alpha^2}$$
$$D_1 = \frac{4}{\alpha} - \frac{6}{\alpha^2}$$
$$D_2 = -\frac{1}{\alpha} + \frac{3}{\alpha^2}. \tag{18}$$

We now can take the potential $\tilde{V}_{rot}$ instead of the true rotational potential V_{rot} and solve the Schrödinger equation for $l \neq 0$ in Eq.(12).

3.2 Applying Nikiforov-Uvarov Method to the Schrödinger Equation

Now, in order to apply the NU−method, we rewrite Eq.(12) by using a new variable of the form $s = e^{-\alpha x}$,

$$\frac{d^2 R_{nl}(s)}{ds^2} + \frac{1}{s}\frac{dR_{nl}(s)}{ds} + \frac{2\mu r_0^2}{\hbar^2 \alpha^2 s^2}\left[(E_{nl} - \gamma D_0) + (2D - \gamma D_1)s - (D + \gamma D_2)s^2\right] R_{nl}(s) = 0. \tag{19}$$

By introducing the following dimensional parameters

$$-\varepsilon_1^2 = \frac{2\mu r_0^2(E_{nl} - \gamma D_0)}{\hbar^2 \alpha^2}, \qquad \varepsilon_2 = \frac{2\mu r_0^2(2D - \gamma D_1)}{\hbar^2 \alpha^2}, \qquad \varepsilon_3 = \frac{2\mu r_0^2(D + \gamma D_2)}{\hbar^2 \alpha^2}, \tag{20}$$

which leads to a hypergeometric type equation defined in Eq.(1):

$$\frac{d^2 R_{nl}}{ds^2} + \frac{1}{s}\frac{dR_{nl}}{ds} + \frac{1}{s^2} \times \left[-\varepsilon_1^2 + \varepsilon_2 s - \varepsilon_3 s^2\right] R_{nl} = 0. \tag{21}$$

After the comparison of Eq.(21) with Eq.(1), we obtain the corresponding polynomials as

$$\tilde{\tau}(s) = 1, \quad \sigma(s) = s, \quad \tilde{\sigma}(s) = -\varepsilon_1^2 + \varepsilon_2 s - \varepsilon_3 s^2. \tag{22}$$

Substituting these polynomials into Eq.(6), we obtain π function as

$$\pi(s) = \pm\sqrt{\varepsilon_3 s^2 + (k - \varepsilon_2)s + \varepsilon_1^2} \tag{23}$$

taking $\sigma'(s) = 1$. The discriminant of the upper expression under the square root has to be zero. Hence, the expression becomes the square of a polynomial of first degree;

$$(k - \varepsilon_2)^2 - 4\varepsilon_1^2 \varepsilon_3 = 0. \tag{24}$$

When the required arrangements are done with respect to the constant k, its double roots are derived as $k_{+,-} = \varepsilon_2 \pm 2\varepsilon_1\sqrt{\varepsilon_3}$.

Substituting $k_{+,-}$ into Eq.(23), the following possible solutions are obtained for $\pi(s)$

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$$\pi(s) = \pm \begin{cases} \left(\sqrt{\varepsilon_3}s - \varepsilon_1 \right), & \text{for} \quad k_- = \varepsilon_2 - 2\varepsilon_1\sqrt{\varepsilon_3} \\ \\ \left(\sqrt{\varepsilon_3}s + \varepsilon_1 \right), & \text{for} \quad k_+ = \varepsilon_2 + 2\varepsilon_1\sqrt{\varepsilon_3} \end{cases} \tag{25}$$

It is clearly seen that the energy eigenvalues are found with a comparison of Eq.(7) and Eq.(8). From the four possible forms of the polynomial $\pi(s)$ we select the one for which the function $\tau(s)$ in Eq.(9) has a negative derivative. Therefore, the function $\tau(s)$ satisfies these requirements, with

$$\tau(s) = 1 + 2\varepsilon_1 - 2\sqrt{\varepsilon_3}\, s,$$
$$\tau'(s) = -2\sqrt{\varepsilon_3}\, . \tag{26}$$

From Eq.(8) we also get

$$\lambda = \varepsilon_2 - 2\varepsilon_1\sqrt{\varepsilon_3} - \sqrt{\varepsilon_3}\, , \tag{27}$$

and also

$$\lambda = \lambda_n = 2n\sqrt{\varepsilon_3}\, . \tag{28}$$

It is seen that the parameter $-\varepsilon_1^2$ has the following form

$$-\varepsilon_1^2 = -\left[\frac{\varepsilon_2}{2\sqrt{\varepsilon_3}} - \left(n + \frac{1}{2} \right) \right]^2 . \tag{29}$$

Substituting the values of $-\varepsilon_1^2$, ε_2 and ε_3 into Eq.(29), we can immediately determine the energy eigenvalues E_{nl} as

$$E_{nl} = \frac{\hbar^2 l(l+1)}{2\mu r_0^2} \left(1 - \frac{3}{ar_0} + \frac{3}{a^2 r_0^2} \right) - \frac{\hbar^2 a^2}{2\mu} \left[\frac{\varepsilon_2}{2\sqrt{\varepsilon_3}} - \left(n + \frac{1}{2} \right) \right]^2 , \tag{30}$$

where

$$\frac{\varepsilon_2}{2\sqrt{\varepsilon_3}} = \frac{1}{a^2\sqrt{\varepsilon_3}} \left[\frac{2\mu D}{\hbar^2} - \frac{l(l+1)}{r_0^2} \left(\frac{2}{ar_0} - \frac{3}{a^2 r_0^2} \right) \right] . \tag{31}$$

The last equation indicates that we deal with a family of the rotating Morse potential. Of course, it is clear that by imposing appropriate changes in the parameters D, a and r_0, the rotational energy spectrum for the any molecules can be calculated by the Pekeris approximation and Nikiforov-Uvarov method as well as other methods [7, 8, 9, 10]. In this study, we calculate the rotating energy values of the Morse potential for the CO and LiH molecules. The explicit values of the energy for the different values of n and l are shown in Tables 1 and 2, for known values of their relevant potential parameters [11, 12, 13].

Let us now find the corresponding eigenfunctions for this potential. Due to the NU−method, the polynomial solutions of the hypergeometric function $y(s)$ depend on the determination

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of the weight function $\rho(s)$ which is satisfies the differential equation $[\sigma(s)\rho(s)]' = \tau(s)\rho(s)$. Thus, $\rho(s)$ is calculated as

$$\rho(s) = s^{1+2\varepsilon_1}e^{-2\sqrt{\varepsilon_3}\, s}. \tag{32}$$

Substituting into the Rodrigues relation given in Eq.(4), the eigenfunctions are obtained in the following form

$$y_{nl}(s) = B_{nl}s^{-(1+2\varepsilon_1)}e^{2\sqrt{\varepsilon_3}\, s}\frac{d^n}{ds^n}\left[s^{(n+1+2\varepsilon_1)}e^{-2\sqrt{\varepsilon_3}\, s}\right], \tag{33}$$

where B_{nl} is the normalization constant. The polynomial solutions of $y_{nl}(s)$ in Eq.(33) are expressed in terms of the associated Laguerre Polynomials, which is one of the orthogonal polynomials, that is

$$y_{nl}(s) \equiv L_n^{1+2\varepsilon_1}(\nu), \tag{34}$$

where $\nu = 2\sqrt{\varepsilon_3}\, s$. By substituting $\pi(s)$ and $\sigma(s)$ into the expression $\phi(s)'/\phi(s) = \pi(s)/\sigma(s)$ and solving the result differential equation, the other part of the wave function in Eq.(2) is found as

$$\phi(s) = s^{\varepsilon_1}e^{-\sqrt{\varepsilon_3}\, s}, \tag{35}$$

or in terms of ν

$$\phi(\nu) = (2\sqrt{\varepsilon_3})^{-\varepsilon_1}\nu^{\varepsilon_1}e^{-\nu/2}. \tag{36}$$

Combining the Laguerre polynomials and $\phi(\nu)$ in Eq.(2), the radial wave functions are constructed as

$$R_{nl}(r) = A_{nl}(2\sqrt{\varepsilon_3})^{-\varepsilon_1}\nu^{\varepsilon_1}e^{-\nu/2}L_n^{1+2\varepsilon_1}(\nu), \tag{37}$$

where A_{nl} is a new normalization constant. It is clearly verified that $R_{nl}(r)$ satisfies the following requirement

$$\int_0^\infty R_{nl}^2(r)dr < \infty.$$

The constant A_{nl} is determined by making this integral equal 1,

$$A_{nl}^2\frac{(2\sqrt{\varepsilon_3})^{-2\varepsilon_1}}{a}\int_0^\infty \nu^{2\varepsilon_1-1}e^{-\nu}\left[L_n^{1+2\varepsilon_1}(\nu)\right]^2 d\nu = 1. \tag{38}$$

The integral in Eq.(38) can be evaluated by using the recursion relation for Laguerre polynomials and then the normalization constant can be found as

$$A_{nl}^2 = \frac{4an!(1+n+\varepsilon_1)^2(2\sqrt{\varepsilon_3})^{2\varepsilon_1}}{(1+n+2\varepsilon_1)!}. \tag{39}$$

Therefore, the simplest radial wave function becomes for $n = 0$:

$$R_{0l}(r) = 2^{2-\varepsilon_1}(1+\varepsilon_1)\sqrt{\frac{an!}{(1+2\varepsilon_1)!}}\,\nu^{\varepsilon_1}\, e^{-\nu/2}. \tag{40}$$

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4 Conclusions

We have presented an approximation for the rotational correction on the Morse potential which leads to analytic calculations for the energy spectrums and wave functions. In these calculations, we have used a new method which is developed by Nikiforov-Uvarov and applied the Pekeris approximation. Our main results are summarized in Eq.(30) and Eq.(37). This new method is tested by calculating the energies of some actual rotational states of the CO and LiH molecules and comparing the results with those of variational and shifted 1/N expansion methods. The method used here is the best advantage than the other methods, such as series solutions, shifted 1/N expansion, supersymmetric approach and Laplace transforms, due to the fact that a systematical one.

References

[1] P. M. Morse, Pyhs. Rev. **34**, 57 (1929).

[2] A. E. DePristo, J. Chem. Phys. **74**, 5037 (1981).

[3] C. L. Pekeris, Pyhs. Rev. **45**, 98 (1934).

[4] A. F. Nikiforov, V. B. Uvarov, "Special Functions of Mathematical Physics" (Birkhauser, Basel, 1988).

[5] G. Szego, "Orthogonal Polynomials", (American Mathematical Society, New York, Revised edition, 1959).

[6] S. Flügge, "Practical Quantum Mechanics I" (Springer-Verlang, Berlin, 1971).

[7] S. H. Dong, and G. H. Sun, Physics Letters **A 314**, 261 (2003).

[8] G. Chen, Physics Letters **A 326**, 55 (2004).

[9] D. A. Morales, Chemical Physics Letters **394**, 68 (2004).

[10] D. Han, X. Song, and X. Yang, Physica **A 345**, 485 (2005).

[11] M. Bag, M. M. Panja, R. Dutt and Y. P. Varshni, Pyhs. Rev. **A 46**, 6059 (1992).

[12] Y. P. Varshni, Can. J. Chem. **66**, 763 (1988).

[13] E. D. Filho, Phys. Lett. **A 269**, 269 (2000).

Table 1: Energy eigenvalues (in eV) for the different values of n and l for CO molecule, with $D = 90540 \ cm^{-1}$, $a = 2.2994 \ \mathring{A}^{-1}$, $r_0 = 1.1283 \ \mathring{A}$ and $\mu = 6.8606719 \ amu$ [11, 13].

n	ℓ	NU Method	Variational	1/N Expansion
0	0	-11.091	-11.093	-11.091
0	5	-11.084	-11.085	-11.084
0	10	-11.065	-11.066	-11.065
5	0	-9.795	——	-9.788
5	5	-9.788	——	-9.782
5	10	-9.769	——	-9.765
7	0	-9.299	——	-9.286
7	5	-9.292	——	-9.281
7	10	-9.274	——	-9.265

Table 2: Energy eigenvalues (in eV) for the different values of n and l for LiH molecule, with $D = 20287\ cm^{-1}$, $a = 1.1280\ \mathring{A}^{-1}$, $r_0 = 1.5956\ \mathring{A}$ and $\mu = 0.8801221\ amu$ [11, 13].

n	ℓ	NU Method	Variational	1/N Expansion
0	0	-2.4287	-2.4291	-2.4278
0	5	-2.4012	-2.4014	-2.3999
0	10	-2.3287	-2.3287	-2.3261
5	0	-1.6476	——	-1.6242
5	5	-1.6236	——	-1.6074
5	10	-1.5606	——	-1.5479
7	0	-1.3774	——	-1.3424
7	5	-1.3549	——	-1.3309
7	10	-1.2957	——	-1.2781